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# ILLINOIS FLUORSPAR

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# ILLINOIS FLUORSPAR

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# ILLINOIS FLUORSPAR

G. C. Finger, H. E. Risser, and J. C. Bradbury

## ABSTRACT

This circular describes in nontechnical form the geology, production, economic aspects, and uses of Illinois fluorspar.

The fluorspar deposits, found principally in Hardin and Pope Counties of southeastern Illinois, occur as fissure fillings in faults and as replacement bodies in limestone. Production comes from underground mines. Modern mills up-grade the raw fluorspar ore to provide a finished product for use in the metallurgical, ceramic, and chemical industries. Lead and zinc are important by-products.

Illinois for many years has been the leading producer of fluorspar in the United States, a position due in part to strategic geographical location with respect to water, rail, and highway transportation, and to consuming industries.

More than 50 percent of the fluorspar produced is used in the chemical industry for the manufacture of hydrofluoric acid, a basic material in production of fluorine chemicals. The metallurgical industry, especially in the open-hearth steel process, consumes about 40 percent of the fluorspar as a fluxing agent. Most of the remaining fluorspar is used as a flux and opacifying agent in the ceramic industry for the manufacture of glass and for enamel coatings on sinks, bathroom fixtures, stoves, refrigerators, signs, and the like.

Fluorine chemicals are useful in aluminum production, atomic energy processing, rocket and missile fuels, water fluoridation, refrigerants, aerosol propellants, plastics, insecticides, fungicides, medicinals, and in many other specialty products.

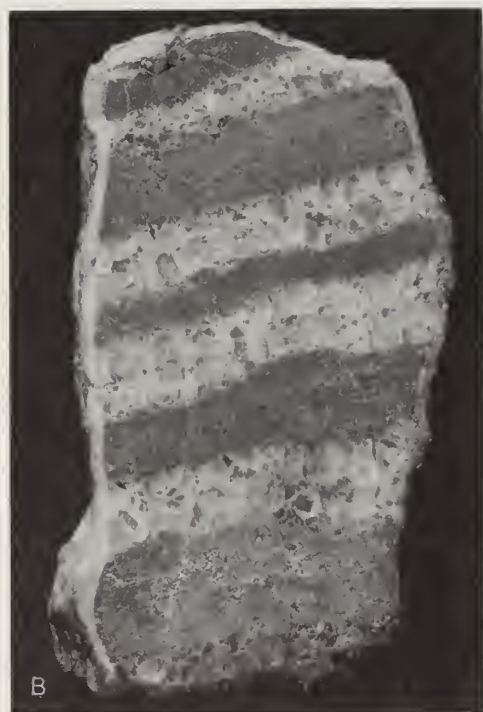
## INTRODUCTION

From the hills of southern Illinois comes a mineral which performs many important and essential functions in modern industry — the mineral fluorspar. In the making of steel, enamels, aluminum, special glasses, and a host of chemicals, Illinois fluorspar plays an important part. For many years the state has been the country's largest producer of this mineral, and modern mines and mills afford a continuing supply and variety of grades of spar to meet the most demanding requirements of industry.

The part of the report on "Geology, Mining, and Milling" was written by J. C. Bradbury, geologist; "Economic Aspects" by H. E. Risser, mineral economist; and "Uses of Fluorspar and Fluorine Chemicals" by G. C. Finger, chemist.

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# PART I

## GEOLOGY, MINING, AND MILLING

The following paragraphs contain a brief, non-technical account of the geology, mining, and milling of Illinois fluorspar. For a more comprehensive and technical treatment, the reader is referred to Weller, Grogan, and Tippie (34). (Numbered references are listed at the end of this report.)

### GEOLOGY

#### Mineralogy

Fluorspar, also called fluorite, consists of two chemical elements, calcium (51 percent) and fluorine (49 percent), and is known chemically as calcium fluoride ( $\text{CaF}_2$ ). It is a glassy mineral with a hardness of 4 and a specific gravity of 3.18. Illinois fluorspar is commonly colorless, white, or grayish, but some of it is purple, pink, blue, green, yellow, or tan. Characteristically, crystals of fluorspar have a cubic shape (pl. 1A), and pockets of such crystals are found in the southern Illinois deposits. However, most of the fluorspar is massive, that is, in a compact body of interlocking crystals.

#### Producing Districts

The fluorspar of Illinois occurs in Hardin and Pope Counties in the extreme southern part of the state. Rosiclare, Cave in Rock, and Elizabethtown are headquarters for the mining industry. Figure 1 shows the distribution of the mining districts.

The main production of the area has come from the Rosiclare vein system, a belt of mineralized faults in the vicinity of the town of Rosiclare, and from the bedded replacement deposits of the Cave in Rock district, a northeast-trending belt of "blanket" deposits about three miles north of the town of Cave in Rock. Prominent outlying areas include the Stewart vein system, just south of Eichorn in western Hardin County, and the Empire district, an area of vein deposits in eastern Pope County about two miles northwest of Eichorn.

#### Vein Deposits

Vein deposits are steeply inclined, sheet-like deposits that occur as fissure fillings along faults, and their width and continuity depend on the degree of openness of the faults in which they were formed. A fault is a crack in the rocks of the earth's surface along which movement has taken place. In the fluorspar area

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### EXPLANATION OF PLATE 1

- A - Specimen of fluorspar from a cavity, showing characteristic cubic crystals. About one-eighth actual size.
- B - Polished specimen of banded fluorspar. Light bands are coarse-grained, darker bands are fine-grained fluorspar. About half actual size.
- C - Polished specimen of banded fluorspar-zinc ore. Light bands are fluorspar, darker bands are sphalerite (zinc sulfide). About half actual size.



Fig. 1 - Principal districts of the fluorspar mining region. Main production has come from 1) Rosiclare district and 2) Cave in Rock district. Others are 3) Goose Creek vein, 4) Lee vein, 5) Hamp mines and vicinity, 6) Empire district, 7) Lusk Creek fault zone, 8) Stewart vein system, and 9) Interstate group and vicinity.

the faults are usually vertical or nearly so, and the rocks on one side of the faults have dropped down whereas those on the other side remained stationary or moved upward. At some places there was also sideward movement along the faults.

The fault surfaces were never perfectly even; instead they were wavy and irregular, preventing a good fit of one side of the fault against the other. As a result, the walls of the fault were pushed apart, producing openings in which fluor-spar veins were later deposited. At the time of faulting, some rock along the fault was crushed and broken.

The amount of vertical movement along a fault also had an important bearing on the formation of ore deposits. For example, a small amount of vertical movement, 25 feet or so, probably would not push the fault walls far enough apart to create large open spaces in which the ore minerals could be deposited. Conversely, along the very large faults that had 1000 feet or more of vertical movement, the crushing and grinding were so intense that few open spaces of suitable size were left for formation of minable ore deposits. However, faults of moderate displacement commonly had less shattering and therefore possessed more favorable characteristics for ore deposition. Within the fluorspar district, faults of 100 to 200 feet displacement generally offered the best conditions for vein deposition.

The exact manner in which the fluorspar veins were formed is not known. Presumably, they were deposited by crystallization from hot, rising solutions that originated deep below the surface of the earth.



## Bedded Deposits

The bedded replacement deposits (fig. 2) generally are flatlying, irregular bodies of ore parallel to the beds of the host limestone. Typically, the deposits are elongate and range from 200 to more than 2500 feet in length and 50 to 300 feet in width. Thicknesses are commonly 4 to 15 feet, with the ore wedging out at the margins.

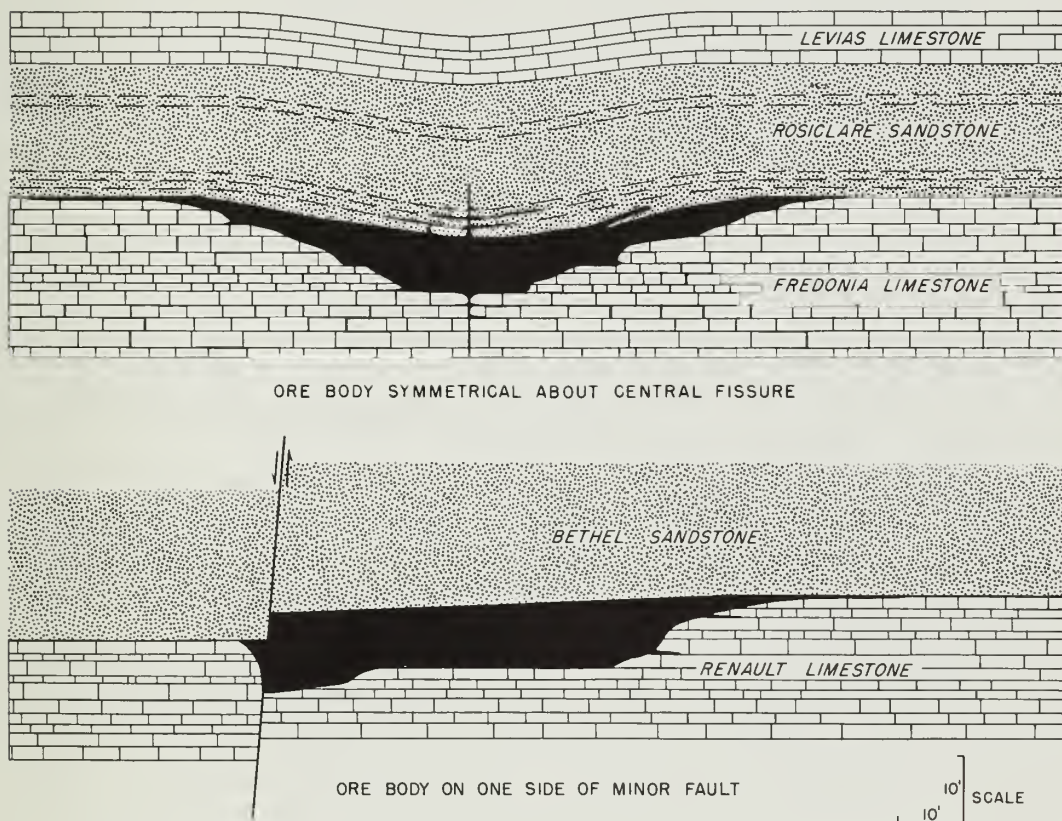


Fig. 2 - Schematic cross-sections of two general types of bedding-replacement fluorspar deposits (from Grogan, 1949).

Unlike the vein deposits, in which the fluorspar simply filled open fissures, the bedded deposits were formed by a chemical reaction between the fluorine-bearing solutions and the limestone in such a way that the calcium carbonate of the limestone was changed to calcium fluoride or fluorite. Probably the reason for this difference in behavior of the solutions was the character of the fracture zones through which they moved.

The vein deposits, it will be recalled, are found in faults of considerable displacement, along which open spaces as much as 30 feet wide were formed. The bedded deposits, on the other hand, follow groups of joint-like fractures or minor faults of a few inches to 20 feet displacement where the amount of movement was not enough to create large openings. Along the larger faults, then, ample space was provided for the mineralizing solutions to deposit their load, but the lack of

open space in the joints and minor faults caused the solutions to move out laterally along bedding planes, or possibly, even through the pores of the less dense layers of rock. The resulting intimate contact between solutions and rock led to chemical reaction between the two and the resulting replacement of limestone by fluorite.

### Mixed Deposits

In addition, a few other deposits, combining features of the bedded and vein deposits, generally occur in faults of small (approximately 25 feet) displacement. The deposits are characterized by a rather narrow (2 to 3 feet) vein with local widenings where certain limestone beds are replaced by fluorspar. On some veins, as the Pierce vein in the Empire district, the favorable bed may be replaced for a length of several hundred feet along the vein.

### Relation of Deposits to Kind of Rock

Just as the character of the faults influences the size or type of deposit, the various kinds of rock also have their effect on the deposits, both vein and bedded. Figure 3 shows the succession of rock formations present in the fluorspar district. In the veins, the best deposits occur where the fault walls are composed of the stronger, or more competent, rocks (limestones and well-cemented sandstones). The weaker, or less competent, formations, such as shale and shaly limestone or sandstone, were easily crushed by movement along the fault and tend to fill rather than create openings.

Because they are strong and competent, the Ste. Genevieve and St. Louis Limestones generally are the most favorable strata for vein deposits. Good vein deposits may be found in higher formations, but because many higher rocks are shaly, the deposits are likely to be of limited size. Some competent rock units exist in these higher beds, but the accompanying incompetent beds tend to plug the fault, causing numerous barren or lean portions along the vein.

The bedded replacement deposits occur chiefly in a relatively small vertical thickness of rock from the base of the Bethel Sandstone downward to the middle part of the Fredonia Limestone (fig. 3). The principal deposits are found at only three favored positions within this 190-foot interval — in the limestone at the top of the Renault Formation, in the top part of the Fredonia Limestone, and near the level of the Spar Mountain Sandstone Lentil, 45 to 60 feet below the top of the Fredonia — possibly because these limestone beds are more pure, more porous, or more fractured than other beds.

### Minerals Comprising the Ore Deposits

The valuable minerals of the fluorspar deposits are fluorite, sphalerite (zinc sulfide,  $\text{ZnS}$ ), and galena (lead sulfide,  $\text{PbS}$ ). The latter two are the common ore minerals of zinc and lead, respectively. The mineral calcite (calcium carbonate,  $\text{CaCO}_3$ ) is common in the deposits but is of little commercial value at present. At some places barite (barium sulfate,  $\text{BaSO}_4$ ) is abundant.

In the veins, fluorite and calcite are the only minerals commonly present. Sphalerite and galena, if present, occur only at scattered places, usually at the margins of the veins, and represent only a minor product of vein mining. Barite has been found at various places but noteworthy concentrations are known in only a few areas. Apparently the last mineral to be deposited during the ore-forming period, it occupies the central parts of fluorspar veins or occurs in narrow fissures next to the veins.

SYSTEM	FORMATION	LITHOL- OGY	DESCRIPTION
PENNSYLVANIAN			Sandstones and shales 700' - 800'
MISSISSIPPIAN			Alternating limestones, shales, and sandstones 800' - 900'
	Cypress- Paint Creek- Bethel		Sandstone; shale or shaly sandstone in middle portion 200' - 240'
	Renault		← Fluorspar bedded deposits
			Limestone 10' - 40'
			Shale and limestone 30' - 50'
	Levias Member		Limestone 10' - 40'
	Rasicleare Member		Sandstone 15' - 45'
	Ste. Genevieve		← Fluorspar bedded deposits
			Limestone 100' - 220'
	Fredania Member		← Spar Mountain Lentic (sandy bed) ← Fluorspar bedded deposits
	St. Louis		Limestone

Fig. 3 - Principal fluorspar-bearing portion of stratigraphic column of the southeastern Illinois fluorspar district. Cross-hatched parts represent horizons most favorable for the occurrence of bedded deposits. The most productive parts of veins generally occur below the shaly Renault Formation.

In the bedded deposits, as in the vein deposits, fluorite is the chief valuable mineral, but sphalerite and galena are important ore minerals in some places. Calcite is less common than in the vein deposits but is abundant locally. Barite is almost entirely absent in some deposits but abundant in parts of other deposits.

The fluorite commonly occurs as alternating coarse- and fine-grained layers in banded ore (pl. 1B) and as massive bodies of various shapes within the orebodies. Where abundant, sphalerite takes the place of the fine-grained fluorite layers in banded ore (pl. 1C). Galena occurs in the coarse-grained layers of banded ore as separate masses one-fourth to 3 inches in diameter. Barite occurs as alternating layers with fluorite in banded ore and also as massive bodies that have filled cavities or replaced limestone or fluorite.

#### MINING

Most fluorspar produced in southern Illinois comes from underground mines, although minor tonnages are produced from open pits in shallow, weathered deposits

where the common types of earth-moving machinery, such as bulldozers, power shovels, and drag lines, are used. Underground mining methods must be suited to the particular type of deposit being worked and, generally, are shrinkage stoping in the vein deposits and room-and-pillar methods in the bedded deposits.

### Vein Mining

In vein mining (fig. 4) a vertical shaft is first excavated in the rock adjacent to the vein. From this shaft a tunnel-like opening, called a cross-cut, is driven horizontally into the vein at a selected depth below the ground surface. On reaching the vein, a drift (horizontal tunnel following the vein) is driven and serves as a haulage level and starting point for shrinkage stoping. The stope (open space made as ore is taken from the vein) is excavated upward from the drift by drilling and blasting.

In wide veins, the roof of the drift is commonly an arch of vein material left in place (fig. 4), but in narrow veins, the roof is made with timbers. The broken ore is drawn from the stope into mine cars through bins and hauled to the shaft for hoisting to the surface. Only enough ore is removed during the stoping operation to give working room to the miners (fig. 4).

Other haulage levels may be driven above or below the initial level, usually at vertical intervals of 100 feet, and stoping is continued upward from one level to the next. If the overlying drift is to be preserved, an arch of unbroken vein material is left in place.

### Mining of Bedded Ore

Bedded fluorspar deposits are mined underground by a modified form of the room-and-pillar method in which the ore is excavated from rooms, and pillars are left between the rooms to support the mine roof. Bedded deposits that are exposed on steep hill slopes can be mined by driving a tunnel, called an "adit," directly into the orebody. Vertical shafts are sunk to those not easily

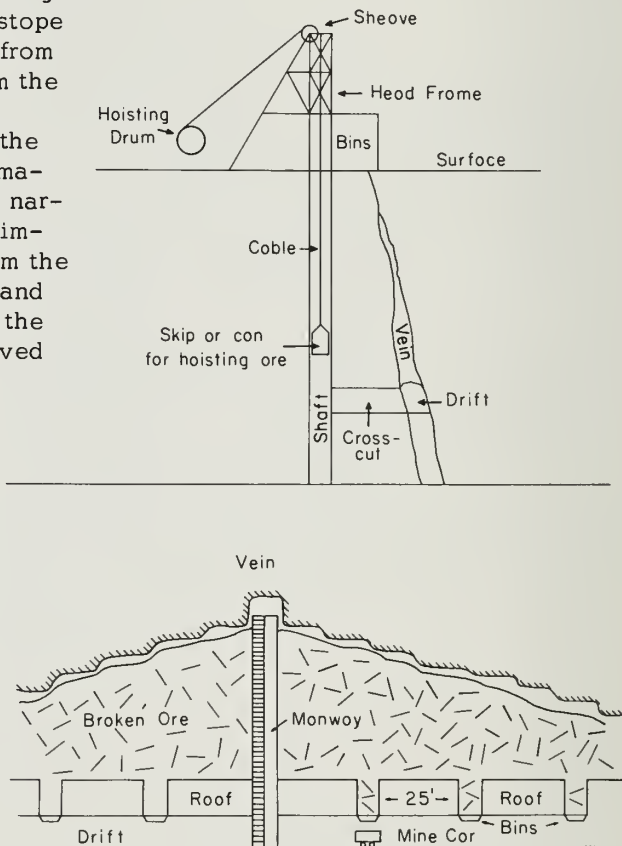


Fig. 4. - Mining in a vein deposit. Top drawing is a section at right angles to the vein showing the general relations of surface installations and underground workings to the vein. Lower drawing is a view parallel to the vein and illustrates the shrinkage stoping method of vein mining. The space between the roof of the drift and the undisturbed vein material is called the "stope."



accessible by such direct means. In either case, a main haulage drift is usually driven along the center of the orebody, and rooms are mined out from it at irregular intervals and continued through the workable deposit. The ore is drilled and blasted, loaded by machines into cars or trucks, and hauled to the mine shaft, or, if an adit mine, to bins or stockpiles on the surface. The larger mines are highly mechanized.

### MILLING

The fluorspar ore, as it comes from the mines, commonly comprises a mixture of fluorspar, calcite, and various amounts of limestone or other rock that are unavoidably mined with it. In addition some of the ore also contains valuable sphalerite and galena. It is usually necessary to rid the ore of the waste calcite and rock and to separate the fluorspar and other valuable minerals.

#### Hand-picking and Washing

A few small mines use hand-picking to separate lumps of fluorspar from the ore in order to get a premium product, but most ore goes through one or more mechanical processes to beneficiate it. The simplest process, washing, is useful in separating spar from contaminating clay. This usually is satisfactory only for the weathered ores and involves the use of a mechanical washing device, known as a log washer, or washing on a vibrating screen or trommel.

#### Jigging

To process their ores, a few small mills use jigging which makes use of the fact that fluorspar is heavier than most waste materials occurring with it. The method employs water as the separating medium. By an up-and-down pulsating action, the lighter material is floated over the sides of the jig cell while the heavier fluorspar remains behind. However, as the specific gravity of fluorspar is not greatly different from that of the waste materials (fluorspar 3.1; calcite 2.7; quartz 2.7; limestone 2.6 to 2.7), jigging does not effect a high degree of separation. Jigging has been used chiefly for producing the lower commercial grades of fluorspar and, until a few years ago, in the larger mills as a primary separation process to get rid of a portion of the waste materials before putting the ore through a subsequent milling operation. Jigging has also been used to separate galena (specific gravity 7.5) from mixed fluorspar-galena ores, but, except in special circumstances, this part of the processing is now done by a more effective method.

#### Heavy Media Separation

A newer and more efficient separation process based on differences in specific gravities is heavy media separation (HMS) by which the ore minerals are separated from waste in a cone containing a suspension of finely ground ferrosilicon in water. The specific gravity of the suspension, or heavy medium, is maintained between 2.55 and 2.62 at the top and 2.85 and 3.1 at the bottom of the cone.

Crude ore is introduced at the top of the cone, and particles having specific gravities greater than that of the medium near the bottom, such as fluoride and the sulfides, sink and are recovered at the bottom of the cone. Particles of lesser gravity such as quartz and calcite are buoyed up and carried away with the overflow from the cone. Ferrosilicon is washed from the ore and waste materials, recovered magnetically, and returned to the cone. The product of heavy media separation may be marketed directly or further processed by flotation.

### Flotation

Most of the higher grades of fluorspar shipped from Illinois are concentrates made by a process called flotation. This process makes use of the property of certain reagents or oily liquids to selectively coat specific minerals. In a mixture of the finely ground ore in water, air bubbles will adhere to the mineral grains thus coated and cause them to float. In practice, a chemical frothing agent is added to the ore-water mixture and air is bubbled through it. The bubbles sweep the selected particles to the surface of the flotation cell where the froth is collected and de-watered by filtering.

Flotation is of much value to the Illinois fluorspar industry because it allows the use of leaner ores and also permits the efficient separation of the valuable lead and zinc minerals, galena and sphalerite, which occur with fluorspar in some deposits.

### Commercial Grades and Specifications

Fluorspar is marketed in three general grades — metallurgical, ceramic, and acid. Metallurgical grades, used chiefly in steel making, specify a certain number of effective units of  $\text{CaF}_2$ , usually expressed as "effective percent of  $\text{CaF}_2$ ." This figure is obtained by subtracting  $2\frac{1}{2}$  times the percentage of silica ( $\text{SiO}_2$ ) from the percentage of  $\text{CaF}_2$  in the fluorspar concentrate. For example, a concentrate assaying 85 percent  $\text{CaF}_2$  and 5 percent  $\text{SiO}_2$  will contain  $72\frac{1}{2}$  percent effective  $\text{CaF}_2$ . The grades most commonly listed in market quotations are 60, 70, and  $72\frac{1}{2}$  percent effective  $\text{CaF}_2$ .

Ceramic and acid grades of fluorspar are of higher purity than metallurgical grades, and specifications are expressed in percentage of  $\text{CaF}_2$ . Ceramic grades generally range from 85 percent to 96 percent  $\text{CaF}_2$ . Acid grade, used chiefly in the aluminum and chemical industries, must contain 97 percent or more  $\text{CaF}_2$ .

### Exploration for Additional Deposits

The ability of Illinois fluorspar mining industry to continue to supply a vitally needed raw material to the nation's industries depends upon a forward-looking exploration program to discover new deposits. In the early days of fluorspar mining in Illinois, the miner had only to sink a shaft or drive an adit into an outcrop of ore. As the mining industry grew and the good surface showings of ore were used up, prospecting solely by underground excavations became too costly, and drills that could penetrate and sample the rock came into general use.

Today, systematic drilling programs are guided by geologists who are trained to evaluate information gained by the study of surface rock exposures and drilling samples. But the future will see the need for even more subtle ore-finding methods. To this end, mining company exploration staffs and Illinois State Geological Survey geologists are constantly on the alert for new ideas on ore occurrence or new methods of exploration.

Geochemical exploration, involving the application of chemical analytical methods to field geology, has been tried with varying degrees of success in recent years by the mining companies and by the Survey. One company is claiming good results in tracing a vein by analysis of soil samples for fluorine.

Various geophysical methods also have been investigated by both government and private interests. The United States Geological Survey, in cooperation with the Illinois State Geological Survey, demonstrated that some faults can be



discovered and accurately located by an electrical method called "earth resistivity." The seismic method, consisting of measurement of the velocity of artificial earthquake waves generated by a small charge of dynamite, has been tried by the Illinois Survey in a limited way and also appears to be capable of detecting and tracing faults.

Photogeologic techniques, used in the district for several years, involve the inspection of pairs of aerial photographs with the aid of a stereoscopic viewer. The three-dimensional effect thus produced helps to emphasize minor differences in topography and vegetative cover, aiding in the mapping of rock structures such as faults. This procedure is reported to be a useful tool in the search for new mineralized belts and is credited by one company with several important discoveries.

Standard field geology methods are being employed by the Illinois Survey in the revision of the 1920 geologic map of the mining district. The availability of new and more accurate topographic base maps, in the process of completion by the United States Geological Survey, and the existence of a wealth of data accumulated by the mining companies through exploration drilling over the last 40 years, make it possible to produce more detailed and accurate maps. Begun in the 1958 field season, the new map, through a more accurate location of faults and in other ways, is expected to be an important aid in the discovery of new deposits in the fluorspar district.

## PART II

### ECONOMIC ASPECTS

The first recorded fluorspar mining in Illinois was in 1842 when a small operation was begun in Hardin County near the site of the present Rosiclare mine (14). Since that year production has been more or less continuous, although shipments from the area apparently did not begin until about 1870. From the beginning Illinois was a major source of production in the United States and for many years has been the principal producer. To date, it has provided more than half the total fluorspar produced within the United States.

Illinois' eminent position as a producer of fluorspar stems primarily from the ready accessibility and strategic geographic location of its deposits that, lying at relatively shallow depths, are readily exploited. Surrounding the fluorspar deposits, and closely linked to them by railway, highway, and waterway networks, are major centers of industrial, chemical, and steel production. Nowhere else within the United States are fluorspar deposits so favorably situated.

Prior to 1888, the United States' consumption of fluorspar was very small and, according to existing records, probably never exceeded 5,000 tons per year. The material was used principally in production of glass, enamel, and hydrofluoric acid, although smaller amounts were used in smelting nonferrous and precious metals. That year the introduction of commercial open-hearth steel production into the United States opened up a new market whose importance quickly overshadowed all former uses.

#### TRENDS IN FLUORSPAR CONSUMPTION

Following the introduction of the open-hearth process, United States' consumption of fluorspar rapidly increased, starting at about 5,000 tons per year in 1888 and reaching a maximum of approximately 645,000 tons in 1953. For more than 60 years the steel industry was the leading consumer of fluorspar, and, until World War II, commonly accounted for 75 to 80 percent of the total quantity consumed. With so large a portion of the total going into steel, the fluorspar industry was vitally affected by the frequent ups and downs of steel production.

Despite the marked increase in the use of fluorspar in steel production over the years, the use for this purpose has failed to keep pace with growth in steel output, especially in the last 30 years. The failure of fluorspar consumption to parallel steel production resulted from improved methods and efficiency which reduced fluorspar usage from 7.4 pounds per ton of open-hearth steel in 1927 to less than 4 pounds per ton in 1957.

From 1927 to 1957, steel production rose from 45,000,000 tons to about 113,000,000 tons per year, for an increase of 151 percent. During the same period, fluorspar consumed in steel manufacturing increased from 138,000 tons to 250,000 tons, or an increase of only 81 percent. After 1957, steel production and fluorspar consumption both decreased owing first to the recession of 1958, and then to the steel strike of 1959.

The lag in consumption of fluorspar in steel manufacture, coupled with a tremendous increase in hydrofluoric acid production during recent years, has caused steel to drop into second place as a consumer of fluorspar. Figure 5 shows changes in the quantities of fluorspar used by various consumer groups in recent years.

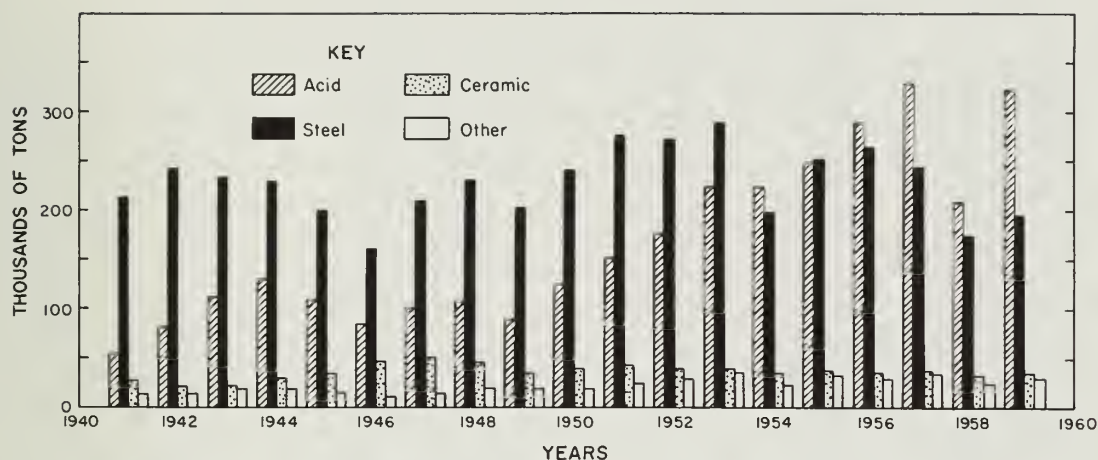


Fig. 5 - United States consumption of fluorspar, 1941-1959, by use

The hydrofluoric-acid industry has long been an important consumer of fluorspar, but with the phenomenal growth of the industry in the last several years the quantity of fluorspar used for this purpose has been rapidly increasing. In only the last decade there has been a three-fold increase in the industry's consumption of fluorspar. In 1959, acid manufacture accounted for about 55 percent of the total fluorspar consumed. Much growth of the hydrofluoric-acid industry stems from the widening use of fluorine chemicals for industrial and other uses. Fluorine compounds are used for insecticides, wood preservatives, welding fluxes, antiseptics, as a concrete hardener, tooth decay preventive, synthetic optical crystals, and many other purposes.

Another reason for the marked expansion in hydrofluoric-acid production is the important role that acid plays in the production of aluminum. The aluminum industry uses hydrofluoric acid to manufacture aluminum fluoride and synthetic cryolite; about 58 pounds of aluminum fluoride and 47 pounds of cryolite, having a combined equivalent of 148 pounds of fluorspar, are used for each ton of aluminum. An increase in aluminum output from 623,000 tons in 1948 to 1,566,000 in 1958 had a pronounced effect on the hydrofluoric-acid production.

The use of fluorspar in ceramics and for miscellaneous purposes has not fluctuated much in recent years. In ceramics, fluorspar is used principally in the manufacture of opal, opaque and colored glass, and to make various colored enamels for coating metal and metalware and ceramic tiles. Miscellaneous uses for spar are as an artificial abrasive and as an additive in portland cement, rock wool, basic refractory cements, and buff face bricks. Ceramics and miscellaneous uses normally account for about 11 percent of total annual consumption.

Fluorspar is marketed in three grades — acid, ceramic, and metallurgical — depending principally on its calcium fluoride content, on the presence of certain mineral impurities, and to some degree on particle size. Table 1, showing the various uses to which fluorspar of the different grades is put, also reveals that there is considerable overlapping of grades in some uses, as, for example, in

Table 1. - Fluorspar (Domestic and Foreign) Consumed in the United States by Grades and Industries, 1957-1958, in Short Tons<sup>a</sup>

Grade and industry	Consumption 1957	Consumption 1958 <sup>b</sup>
Acid grade:		
Hydrofluoric acid	328,672	258,935
Glass	3,221	3,916
Enamel	118	125
Welding rod coatings	819	810
Nonferrous	131	25
Special flux	1,763	2,137
Ferroalloys		
Primary aluminum		
Total	334,724	265,948
Ceramic grade:		
Glass	27,899	25,123
Enamel	4,314	4,776
Welding rod coatings	1,154	200
Nonferrous	118	5,339
Special flux	7,983	1,134
Ferroalloys		
Total	41,468	36,572
Metallurgical grade:		
Glass	1,017	824
Enamel	800	88
Welding rod coatings	343	164
Nonferrous	5,123	1,773
Special flux	2,723	1,467
Ferroalloys		
Primary magnesium		
Iron foundry	15,382	12,883
Basic open-hearth steel	212,304	150,328
Electric-furnace steel	30,376	24,033
Bessemer steel	428	147
Total	268,496	191,707
All grades		
Hydrofluoric acid	328,672	258,935
Glass	32,137	29,863
Enamel	5,232	4,989
Welding rod coatings	2,316	1,174
Nonferrous	5,372	7,137
Special flux	7,959	257
Ferroalloys	1,981	1,691
Primary aluminum	2,529	2,790
Primary magnesium		
Iron foundry	15,382	12,883
Basic open-hearth steel	212,304	150,328
Electric-furnace steel	30,376	24,033
Bessemer steel	428	147
Total	644,688	494,227

<sup>a</sup> Source: United States Bureau of Mines<sup>b</sup> Glass, enamel, and other (including welding rod coatings, nonferrous, special flux, and ferroalloys), partly estimated from sample canvass of consumers who accounted for more than 95 percent of total usage in 1957.

Table 2. - Fluorspar Shipments from Illinois Mines

Year	Tons	Value	Year	Tons	Value
1930	44,134	\$ 836,473	1945	147,251	\$5,014,807
1931	28,072	468,386	1946	154,525	5,493,642
1932	9,615	156,279	1947	167,157	6,148,654
1933	36,075	543,060	1948	172,561	6,322,246
1934	33,234	567,396	1949	120,881	4,621,733
1935	44,120	685,794	1950	154,623	6,110,765
1936	82,056	1,525,606	1951	204,328	9,294,703
1937	78,664	1,730,585	1952	188,293	9,481,223
1938	35,368	751,227	1953	163,303	8,567,026
1939	75,257	1,638,693	1954	107,830	5,989,219
1940	104,698	2,313,747	1955	166,337	7,838,471
1941	133,333	3,047,247	1956	178,254	8,469,450
1942	161,949	4,306,750	1957	169,939	8,827,171 <sup>a</sup>
1943	198,789	6,292,789	1958	152,087 <sup>a</sup>	7,931,000 <sup>a</sup>
1944	176,259	5,954,991			

a Subject to revision.

glass making and in enamel, where all three grades find some use. Conversely, for making steel or hydrofluoric-acid only one grade is suitable. Metallurgical fluor-spar used in steel furnaces must be of gravel or lump size to perform satisfactorily as a flux. The consumers of acid grade fluorspar require a product that is finely ground and of high purity.

#### PRODUCTION TRENDS

United States production of fluorspar rose from 234,000 tons in 1940 to 301,000 tons in 1950 and to almost 330,000 tons in 1956 and 1957. By 1958 it had fallen to 320,000 tons and in 1959 was only 178,000 tons. The growth in fluorspar production has not paralleled the increase in consumption because of the foreign imports. The effect of the imports has been only partially offset by tariffs and by the United States Government stockpiling program.

United States reserves of fluorspar were estimated in 1956 by the United States Geological Survey to be 22.6 million tons (3), an amount approximately 28 times the 1957 production. Reserves in the Illinois-Kentucky fluorspar district are estimated at 8 million tons.

Of the total fluorspar produced annually within the United States, each year Illinois accounts for about half. In 1958, Illinois led in production with 152,087 tons, followed by California with a production of 59,464, Montana with 53,654, and Kentucky with 25,861 tons. Other producing states during 1958 were Utah with 16,109 tons and Nevada with 12,338 tons. Table 2 gives the annual production by Illinois mines from 1930 through 1958.

The Illinois fluorspar output comes from numerous mines ranging in size from those whose production is only a few hundred tons per year to those producing tens of thousands of tons annually. In general, the output of the small mines is sold to larger operators who have facilities for upgrading the raw mine product, but in some instances, the small mines sell directly to markets that can use fluorspar in the larger sizes and of purity obtained through hand sorting. The larger producers operate mills where the run-of-mine material is crushed or ground and processed to remove impurities either by gravity means or by flotation.



Table 3. - Fluorspar (Domestic and Foreign) Consumed in the United States, by States, in 1957-1958, in Short Tons<sup>a</sup>

State	1957	1958 <sup>b</sup>
Alabama, Georgia, North Carolina and South Carolina	12,268	10,155 <sup>c</sup>
Arkansas, Kansas, Louisiana, and Oklahoma	88,622	29,096
California	35,985	12,621
Colorado and Utah	22,944	17,607
Connecticut	585	747
Delaware and New Jersey	79,275	120,944
Florida, Rhode Island, and Virginia	1,059	698
Illinois	97,454	62,974
Indiana	33,451	25,307
Iowa, Minnesota, Nebraska, South Dakota, and Wisconsin	4,948	3,828 <sup>d</sup>
Kentucky	30,111	29,197
Maryland	5,494	5,330
Massachusetts	443	324
Michigan	20,453	14,594
Missouri	4,340	3,738
New York	20,204	13,832
Ohio	72,151	58,360
Oregon and Washington	1,686	670
Pennsylvania	82,882	55,164
Tennessee	1,058	499
Texas	21,221	15,848
West Virginia	8,054	5,924
Undistributed	-	6,770
Total	644,688	494,227

<sup>a</sup> Source: United States Bureau of Mines.

<sup>b</sup> Consumption partly estimated from sample canvass of consumers who accounted for more than 95 percent of total usage in 1957.

<sup>c</sup> Alabama, Georgia, and South Carolina.

<sup>d</sup> Iowa, Minnesota, and Wisconsin.

Large quantities of fluorspar formerly were cleaned by jigs. At present most mills clean fluorspar in gravel size by heavy-media separation. The coarse product of this operation can be used as metallurgical spar, but more often is further cleaned and up-graded by flotation.

The flotation process yields a finely ground concentrate of high purity and uniform quality that is used in acid manufacture, ceramics, or other applications where the fine size is not a disadvantage. It is not generally suitable for open-hearth steelmaking, but in some instances briquetted or pelletized fine material forms a suitable product for such use.

Almost 90 percent of the finished fluorspar produced in Illinois is shipped in the form of flotation mill concentrates. About 60 percent of the fluorspar shipped from Illinois mines normally goes into the manufacture of hydrofluoric acid. Steel manufacture and ceramic use accounted for about 8 percent each, and the remainder serves miscellaneous purposes.



## MARKETING

Shipments of fluorspar from Illinois mines generally enter the market through one of three principal channels. Some mines are captive operations whose output normally goes directly to the consuming plants of the parent organization. Producers having no affiliations usually sell the major portion of their product through a sales agency or other organization which maintains contact between the producer and potential consumers. A third way in which fluorspar may be marketed is by contract or by direct contact between the producing firm and the purchaser. The output of small mines is mainly sold to larger producers who sell it directly or process it before it enters the market.

Because of its many uses, fluorspar is consumed in many places throughout the United States. At least 37 states reported consumption during 1957 and 1958 as shown in Table 3. Those states containing steel and hydrofluoric acid producing plants account for almost 90 percent of total fluorspar consumption.

Figure 6 shows the location of major steel plants and hydrofluoric acid plants in 1957. A concentration of these plants along the Great Lakes and inland waterways is apparent. Of the total fluorspar used in the United States during 1958, five states — Delaware, New Jersey, Illinois, Pennsylvania and Ohio — accounted for 60 percent. Each of these five states produces steel, and steel production consumes more than half of the total fluorspar used within these states. In addition to steel plants, all these states also contain hydrofluoric-acid plants.

The proximity of the Illinois fluorspar deposits to the major consuming areas places them in an extremely favorable position to serve the entire region.

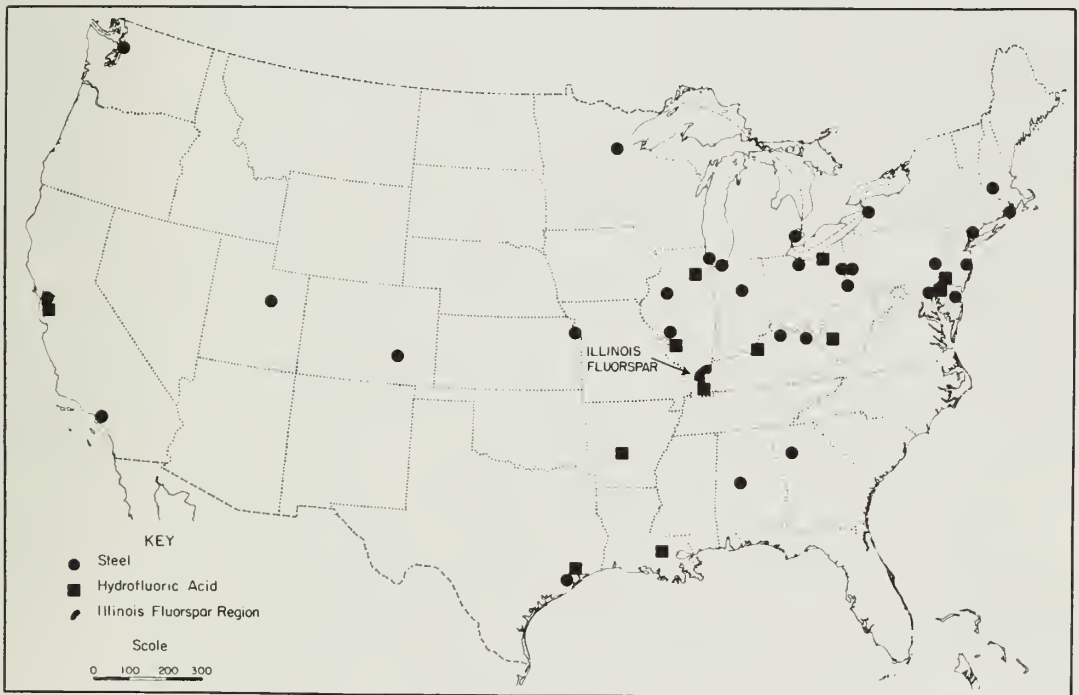


Fig. 6 - Location of steel and hydrofluoric-acid plants, 1957

Fluorspar may be moved from mine to market in any of several ways. Shipments of the larger metallurgical-grade sizes of fluorspar commonly are made in open-type railroad cars or open barges; bulk shipments of the finer sizes are transported in boxcars or covered hoppers. Finely ground fluorspar also is shipped in paper bags usually holding 100 pounds. Truck shipments are either in bulk or in bag. Loading docks on the Ohio River, a short distance from the fluorspar operations, are used to transfer fluorspar to barges for shipment up or down stream. Barges of several hundred ton capacity are used for such shipments.

#### SUMMARY

Production of fluorspar in Illinois and other states is currently limited by competition from foreign imports. Production figures in Table 2 indicate that Illinois possesses a capacity to produce far more fluorspar than is currently produced. Should an interruption occur for any reason in the large quantities of fluorspar entering the United States from outside sources, United States industry would quickly become critically dependent upon the output Illinois can provide. Sudden demands for increased production, however, can be met by the mining industry only if productive capacity is maintained in a high degree of readiness.

# PART III

## USES OF FLUORSPAR AND FLUORINE CHEMICALS

### DIRECT USES OF FLUORSPAR

#### Hydrofluoric Acid Manufacture

The chemical industry, the largest consumer of fluorspar, in 1959 (23) used 324,500 tons of acid spar, or 55 percent of the total fluorspar consumed. For the same year, on the basis of 2.4 tons of spar yielding 1 ton of acid, the production of hydrofluoric acid was estimated at 135,000 tons (29), almost a 300 percent increase in a decade. As hydrofluoric acid is a key chemical in a rapidly growing fluorine chemical industry, its future is most promising. The direct and indirect uses are discussed under uses of fluorine chemicals.

Two types of hydrofluoric acids are commercially available — aqueous and anhydrous. The aqueous acid is a water solution of hydrogen fluoride, whereas commercially the anhydrous product is labelled as such when the moisture content is very low, usually less than 5 percent. The anhydrous product is known in trade language as HF or anhydrous HF (also AHF), or by the misnomer of anhydrous hydrofluoric acid. From a chemical standpoint these two products exhibit marked differences in properties and may be considered as two different chemicals. Both are made by the same basic reaction, namely by the reaction of acid spar with sulfuric acid in heated kilns or retorts.



For many years aqueous hydrofluoric acid has been prepared by absorbing the hydrogen fluoride gases from a retort in water in suitable lead cooling and absorbing towers. By recycling or redistilling the absorption liquors various strengths of acid up to 60 percent were prepared. Acids below 60 percent are shipped in lead, rubber, and more recently in polyethylene containers; for acids of 60 percent and higher, steel containers are used. In modern practice, aqueous acid is prepared by dilution of the anhydrous product to the desired strength, usually at the time a purchase order is received. This has simplified the storage problem because the anhydrous product can be stored in steel.

Anhydrous acid is made by the same general reaction but under more rigidly controlled conditions (19, 29). The generator is ordinarily a horizontal steel kiln that revolves and is heated externally, usually by direct fire. Finely ground acid spar is mixed with a slight excess of strong sulfuric acid in a hopper and fed continuously into one end of the generator. A large vent pipe serves as a collector for the HF and other gaseous products. At the opposite end of the generator, calcium sulfate as a waste product is usually expelled by a screw drive into water.

The composition of the hot gaseous mixture from the generator is about 95 percent HF, 4 percent air, and 1 percent impurities such as  $\text{H}_2\text{SO}_4$ ,  $\text{SiF}_4$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , and  $\text{SO}_2$ . Aluminum fluoride, synthetic cryolite, and some other fluorides can be prepared directly from this gas. For anhydrous acid, the gas is put through a purification process. The gaseous mixture is cooled and absorbed countercurrently in a tower with a weak cycle sulfuric acid to a 70 percent HF concentration. Upon distillation of the concentrated acid, the water remains with the sulfuric acid residue, and the HF is collected as a distillate. Redistillation in a suitable column separates the low-boiling  $\text{SiF}_4$ ,  $\text{CO}_2$ , and  $\text{SO}_2$  from the higher boiling HF (boiling point  $19^\circ \text{C}$ ).

To avoid contamination of the atmosphere, the exit gases may be passed into water absorption towers where the  $\text{SiF}_4$  is converted into fluosilicic acid ( $\text{H}_2\text{SiF}_6$ ). This same acid is recovered on a tonnage basis as a low-cost by-product in the phosphate fertilizer industry.

The anhydrous HF is stored in steel containers, and a purity as high as 99.95 percent HF is available. The current price is 18 cents per pound in carload lots (April 1960). It must always be remembered that hydrofluoric acid is a highly corrosive and hazardous chemical. However, in view of the tremendous tonnages that are being produced, it is obvious that the handling of it has been perfected to a routine operation.

In the manufacture of 1 ton of HF, about 5 tons of fluorspar and acid are required, and about 4 tons of calcium sulfate is formed as waste product. About 2.4 tons of acid spar is required to produce a ton of HF, according to the Bureau of Mines; however, it is suspected that some plants may use approximately 2.2 tons and recent technological advances may lower the figure still further.

The sulfuric acid is usually a commercial 96-percent grade, and a 5 to 10 percent excess is used. As the quality of the acid fluorspar is very important, the specifications are quite rigid. A typical specification is not less than 97 percent  $\text{CaF}_2$ , not more than 1 percent  $\text{SiO}_2$ , 0.05 percent S, 1 percent moisture, and a minimum of calcium carbonate. The relation of  $\text{CaF}_2$  content to HF yield is obvious. Reasons for the other items are: each part of  $\text{SiO}_2$  causes a loss of  $1\frac{1}{3}$  parts of HF as  $\text{SiF}_4$ , sulfur causes process difficulties, moisture affects efficiency, calcium carbonate wastes sulfuric acid, and the  $\text{CO}_2$  causes foaming. It is essential also that the spar be finely ground as it influences the rate of reaction with sulfuric acid.

## Metallurgy

### Steel

Agricola (16) in 1556 mentioned the use of fluorspar as a flux in metallurgy. Owing to this early use the name fluorspar was coined from the Latin, literally meaning the rock that flows.

Today the steel industry is the second largest user of fluorspar, consuming about 40 percent (33) in the form of metallurgical spar. The spar functions as a fluxing agent and may assist also in the refining process. It is used in the basic open hearth, electric furnace, and Bessemer steel processes. The Bessemer process, with a consumption of about 500 tons per year, is a minor consumer.

Basic open-hearth steel (25) normally consumes about 80 percent of the metallurgical spar. The spar in granular form is spread on the furnace floor at the start; after the smelting operation is under way additional spar is shoveled into the furnace in such a way as to be uniformly spread over the slag. Depending on economic conditions, as much as 10 pounds per ton of steel may be used, but the average is about 5 pounds. Annual records show that the average per ton has been decreasing. The spar gives fluidity to the slag, thus resulting in a better steel recovery and lower fuel cost. It also causes the solid lime lumps to dissolve more rapidly in the slag so that a maximum amount of lime is available for the most effective removal of sulfur and phosphorous from the metal.

The furnace gases, as in most metallurgical and foundry processes using fluorspar, may contain considerable quantities of  $\text{SiF}_4$  formed by the reaction of the spar with silica ( $\text{SiO}_2$ ). Severe cases of air pollution by such fluoride fumes are known (3), causing damage to crops and animals, thus necessitating an expensive



fume catching system. Perhaps in time a process will be developed that will recover the lost fluorine for reuse as a flux.

Electric furnace steel uses about 14 to 40 pounds (17) of spar per ton of steel. Only about 10 percent of the metallurgical spar is consumed in this industry. As the demand for special steels is increasing it is expected that the demand for spar also will increase. This industry prefers the higher grade metallurgical spar.

Typical metallurgical grade specifications are a minimum of 60 percent effective  $\text{CaF}_2$ , not more than 0.30 percent sulfide sulfur nor more than 0.25 to 0.50 percent lead. Silica is objectionable because one part requires 2.5 parts of  $\text{CaF}_2$  to flux it; therefore, the silica percentage is multiplied by 2.5 and deducted from the actual  $\text{CaF}_2$  content to get the effective  $\text{CaF}_2$ . Seldom more than 5 percent silica is allowable. Barite ( $\text{BaSO}_4$ ) is objectionable because it decreases fluidity of the slag.

Most steel producers purchase the spar in a gravel size passing through a 1-inch to  $1\frac{1}{2}$ -inch mesh screen and not more than 15 percent fines. Some spar producers can merchandise a pellet the size of a peach seed made from flotation concentrates. Occasionally other sizes may be specified.

### Foundries

In 1959 about 13,000 tons of metallurgical grade spar was used as a flux by iron foundries, primarily in the production of fine grade castings, as for example automotive engines. The spar causes the charge to melt more rapidly, aids in removal of sulfur and phosphorous, gives a more liquid slag, minimizes lime accumulation at air inlets, and gives a cleaner drop at the end of the pouring period. Cleaner, more malleable, and higher tensile strength castings are reported.

An average of 15 to 20 pounds of spar per ton of metal is added to the cupola as lumps, and about 3 percent of ground spar per ton of metal may be added to the ladle. The basic open hearth steel specifications on spar apply to foundry practice. In the cupola, a lump material ranging from nut size and up is used, whereas in the ladle a ground material is preferred.

Domestic mills provide 1 by  $1\frac{1}{2}$ -inch foundry lump in 60 percent effective grade. Most of the larger sized lump is hand sorted.

### Ferroalloys

A ferroalloy is a special alloy of iron with a high proportion of another element such as chromium, manganese, molybdenum, silicon, titanium, tungsten, vanadium, and others. These alloys are identified in commerce as ferrochromium, ferromanganese, and so on. For the most part, they are added in limited amounts to iron and steel melts to function as 1) scavengers and deoxidizers, and 2) for conferring special properties (such as toughness, hardness, corrosion resistance) on a finished steel. Most of them are produced in an electric furnace, and fluorspar is added as a fluxing agent.

The amount and grade of fluorspar added varies widely from plant to plant, type of steel produced, and economic conditions. The consumption will vary from 1 to more than 200 pounds per ton of ferroalloy. A fine size is desired for uniform distribution in the furnace. All grades of spar are used, although the higher grades are preferred.

### Special Fluxes

The category of special fluxes includes a variety of fluxes used in the refractory, aircraft, and welding industries, and in some chemical processes. All

grades of fluorspar are used, and a ground material is desired. In 1957 about 8,000 tons, or about 1.2 percent of the fluorspar consumed, was channeled to the aforementioned customers.

### Welding Rod Coatings

Fluorspar, along with many other fluorides, finds extensive use in welding fluxes and welding rod coatings. The function of a flux in welding is to act as a surface cleansing agent and also to protect the surface from oxidation or burning. Generally, the flux is prepared by melting the components to a homogeneous mixture, after which it is cooled and then ground. For coating welding rods a binder is added. When fluorspar is used, the fluorspar content in the composition ranges from 2 to 50 percent.

About 50 percent of the fluorspar used in coatings is ceramic grade, 35 percent is acid spar, and the remainder is metallurgical grade. A finely ground material is specified.

### Primary Aluminum (15, 24)

Fluorspar is added to the cryolite bath of the aluminum reduction cell as a flux to lower the freezing point. In normal operation, the molten electrolyte contains 6 to 10 percent  $\text{CaF}_2$  and the temperature is held at 950 to 980° C. After a cell is operating, very little fluorspar as such is needed to balance the slight mechanical losses. About 600 tons of spar was used in this manner in 1957.

A ground, acid grade spar is preferred because impurities affect the quality of the aluminum metal and the efficiency of the cell. Iron and silicon contaminate the metal and also form volatile fluorides. Lead and zinc appear in the metal, and sulfur reduces cell efficiency and also forms sulfur gases.

### Smelting: Magnesium, Zinc, and Other Metals

A small amount of ground, metallurgical spar is used as a flux in magnesium reduction. It is likely that some spar also is used in resmelting and casting of the metal.

Zinc smelting (private communication, 1959, William Coolbaugh, metallurgist) by the horizontal retort process is benefitted by the addition of fluorspar. The furnaces are charged with a mixture of 16 pounds of powdered, ceramic spar per ton of sintered zinc ore. The spar serves as a flux and increases the yield and production of zinc metal from the ore. For this purpose, a spar of 88 to 90 percent  $\text{CaF}_2$  and not more than 1 to  $1\frac{1}{2}$  percent moisture are satisfactory.

Minor amounts of fluorspar are reported to be used as a flux in the smelting and refining of antimony, copper, chromium, gold, lead, silver, tin, nickel, and others.

Outside of magnesium, consumption of fluorspar by the preceding nonferrous metals was about 7,000 tons in 1958. Metallurgical spar is generally specified, although some of the acid and ceramic grades also are used.

### Ceramics

#### Glass

The glass industry is a stable consumer of fluorspar, demanding about 30,000 tons per year. The spar is used as a flux and opacifier. Clear glass has the least



amount of spar in its formulation, whereas opal and colored glass demand a larger quantity to obtain opaqueness. Depending on the glass desired, 50 to 500 pounds of ground spar are used for each 1000 pounds of sand in the glass batch. Examples of opal glass are lamp bulbs, globes, shades, toilet and medicinal containers, and many other items. Frequently other fluorides are added along with spar in glass formulations.

About 85 percent of the spar used by the glass industry is ceramic grade; the remainder is almost entirely acid spar. A ground fluorspar is required and is classified as coarse (55 percent passing a 100-mesh sieve), fine, and extra fine.

A typical specification for No. 1 ceramic is not less than 95 percent  $\text{CaF}_2$ , not more than 3 percent  $\text{SiO}_2$ , 1 percent  $\text{CaCO}_3$ , and 0.12 percent  $\text{Fe}_2\text{O}_3$ . Only traces of lead, zinc, barium, and sulfur are permitted. Iron gives a green or yellow tint. As the calcite is converted to lime in the glass furnace, an excess will cause brittleness of the glass and also difficulty in formula control. When specifications differ from the above, most fluorspar producers can meet the demands of the customer.

### Enamel

Enamels and glazes are low-melting glasses used for coating cast iron, steel, and other metals. Fluorspar and other fluorides serve as fluxes in lowering the melting point of the glass melt and also give opacity to the finished coatings. About 5,000 tons of fluorspar per year are used in this manner. Products of this industry are prefabricated metal buildings and store fronts, bath tubs, lavatories, sinks, refrigerators, stoves, signs, artware, and many other common items.

The fluorspar or fluoride content of enamels ranges from 0 to 15 percent. A small percentage will lower the melting point, but opacity requires a higher percentage, usually 6 percent. The ceramic grades are generally specified, although small amounts of the other grades are purchased.

Specifications on the spar for enamel or glazing purposes are much the same as for glass, and for the same reasons. However, there is a tendency to specify a higher quality ceramic spar and a finer screen size.

### Water Fluoridation

One part per million of fluorine in drinking water is the desired concentration in the fluoridation of municipal water supplies. Various fluorine chemicals are being used for fluoridation and not until recently was it possible to use fluorspar, the lowest price fluoride available. The very low solubility of fluorspar in water was the deterrent. In the late 1950's Maier and Bellack (22), Division of Dental Public Health, United States Public Health Service, Washington, D. C., developed a controlled fluoridation process, based on the reaction of alum salts with fluorspar to form soluble fluoride. Since 1956 the demonstration plant at the Bel Air, Maryland, water supply has been proving the practicability of the process. In 1958 a similar plant was installed at Rosiclare, Illinois, with equal success.

A finely ground spar with a high  $\text{CaF}_2$  content is required. In terms of ceramic grade spar (95 percent  $\text{CaF}_2$ ), it is estimated that 18 pounds of fluorspar will fluoridate one million gallons of water.

Regarding cost (11), fluoridation with fluorspar is estimated at \$0.03 per capita per year as against \$0.10 with other presently used fluorides.

## Miscellaneous

## Portland Cement (1, 26)

It is common practice in Germany (13) in manufacturing portland cement, to add 1 to 5 percent of low grade fluorspar to the raw cement mix. The fluorspar lowers the sintering temperature and acts as a mineralizer. In the United States very little spar is used in the cement industry. However, domestic cement manufacturers may benefit from research now in progress on the use of fluorspar as a mineralizer in promoting formation of tricalcium silicate at lower clinkering temperatures. The success of this will mean lower fuel costs, increased kiln capacity, and a longer life for the kiln liner.

Some western cement firms are adding fluorspar to their raw material as an aid in the volatilization of potassium and sodium salts during the clinkering process. Before the development of the domestic potash deposits, the flue gases of the cement industry were an important source of potash. It appears that a finely ground spar of the low metallurgical grade and lower is used.

## Calcium Cyanamide (2, 18)

Calcium cyanamide ( $\text{CaCN}_2$ ) is produced by reacting nitrogen with calcium carbide. In the Frank-Caro electrothermal process (2) about 2 to 3 percent of finely ground fluorspar is added to the calcium carbide to lower the fusion point and increase the velocity of the reaction. The fluorspar must have less than 0.1 percent moisture and must contain a minimum of 90 percent  $\text{CaF}_2$ . Annual production of calcium cyanamide in North America is more than 200,000 tons. It is used as a fertilizer, cotton defoliant, and in the manufacture of melamine resins, sulfa drugs, explosive propellants, and other synthetic organic nitrogen chemicals.

## Mineral Wool

The presence of 1 to 2 percent of acid or ceramic grade spar in certain rock-wool melts will give greater fluidity at a given temperature and a smaller fiber diameter (21) to the final product.

## Brick Stain Inhibitor

The principal contributor to yellow, green, or brown efflorescent stain on light-colored face brick is vanadium. A small percentage of fluorspar added to the clay mix will inhibit this efflorescence to varying degrees, depending on the clay (12).

## Binding Material

A small amount of fluorspar is used as a binder in abrasives and high-temperature brick.

## Optical Lenses

Because clear fluorspar has a low index of refraction, high ultraviolet transmission, and low dispersion, it is used in optical lenses for scientific instruments. As clear, natural crystals are very rare, large artificial crystals (28) are now produced by controlled cooling of a melt of semi-optical grade of spar.

To reduce reflection on optical lenses and prisms, a very thin film of such fluorides as  $\text{LiF}$ ,  $\text{MgF}_2$ ,  $\text{CaF}_2$ , and others can be used (27).

#### Dental Cements

Some dental cements in their composition contain 10 to 15 percent fluorine (27) as  $\text{CaF}_2$  and  $\text{NaF}$ .

#### Jewelry

Colored spar finds some use as a gemstone in jewelry and stone ornaments. Wealthy Romans of 2,000 years ago treasured their goblets of fluorspar from Parthia. The Mound Builder aborigines in America carved crude figures from fluorspar. Many beautiful goblets, urns, and vases of native spar were cut and polished in the 1700's and 1800's in England. A small amount of very pretty jewelry is still produced near Castleton in the Derbyshire District of central England.

### USES OF FLUORINE CHEMICALS

#### Hydrofluoric Acid

The fluorine chemical produced in largest quantities is hydrofluoric acid ( $\text{HF}$ ), an important chemical for two reasons: 1) it is used in nonfluorinating processes as a catalyst, reaction medium, metal pickling agent, and in many other ways, and 2) it is a key chemical in almost all fluorine chemical processes. Stuewe (29) has written a review on the manufacture and uses of  $\text{HF}$ .

Aqueous hydrofluoric acid is used in the manufacture of many inorganic fluorides and acid fluorides; in frosting, etching, and polishing of glass; as an antiseptic in breweries and distilleries; electroplating; cleaning of copper and brass; pickling and galvanizing metals; removal of efflorescence from stone and brick; extraction of tantalum and columbium; in the making of filter paper and carbon electrodes; removal of silica from graphite, and in acidizing oil wells to increase oil production.

Anhydrous  $\text{HF}$  is a versatile and useful chemical. Not only can it advantageously replace aqueous acid in many instances, it has many special applications where it is used in large tonnages. It is especially useful in organic chemistry for fluorination, hydrofluorination, polymerization, esterification, catalysis, alkylation, reaction medium, nitration, sulfonations, and many other processes.

The uses and consumption of  $\text{HF}$  in 1957 are given in table 4. About 75 percent of the  $\text{HF}$  consumed was used in the manufacture of four commodities. The large  $\text{HF}$  consuming industries for the most part produce their own  $\text{HF}$ , with the result that only about 25 percent of the  $\text{HF}$  consuming market is open to merchant producers.

#### Aluminum Fluoride and Synthetic Cryolite

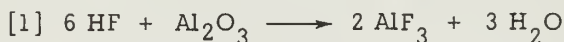
Practically all of the aluminum fluoride ( $\text{AlF}_3$ ) and most of the synthetic cryolite ( $\text{Na}_3\text{AlF}_6$ ) are used as a flux and electrolyte in the production of primary aluminum. About 58 pounds of  $\text{AlF}_3$  and 47 pounds of  $\text{Na}_3\text{AlF}_6$  are used per ton of primary aluminum (32). In the electrolytic refining of primary aluminum to super pure aluminum, the electrolyte is essentially a mixture of cryolite, aluminum fluoride, and frequently barium fluoride (24).

Table 4. - Consumption of HF in 1957<sup>a</sup>

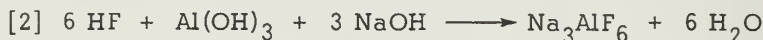
Use	HF (short tons)	Percent of total
Aluminum fluoride	40,000	29.6
Fluorocarbons	38,500	28.5
Uranium production	16,000	11.8
Synthetic cryolite	13,000	9.6
Conversion of salts	7,500	5.6
Stainless steel	7,000	5.2
Petroleum alkylation	6,000	4.5
Special metals	3,000	2.2
Etching and frosting	2,000	1.5
Others	2,000	1.5
Total	135,000	100.0

<sup>a</sup> Source: Stuewe (1958).

Aluminum fluoride generally is prepared by the reaction of HF with alumina as in equation [1].



If synthetic cryolite is desired, an alkaline solution of alumina is reacted with HF as in equation [2].



An alternate source of these fluorides, especially synthetic cryolite, is the silicofluoride route. This will become increasingly important as the phosphate fertilizer industry produces large tonnages of low-cost silicofluoride by-product.

A small amount of aluminum fluoride and appreciable quantities of synthetic cryolite are used as fluxes and opacifiers in ceramics and in welding fluxes. Cryolite also is used as an insecticide.

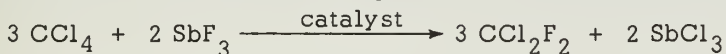
#### Fluorocarbons

The terms fluorocarbons and fluorochemicals have been coined to define carbon compounds containing fluorine. These materials are used as refrigerants, aerosols, plastics, dielectrics, lubricants, coolants, wetting agents, fire extinguishers, and for many other purposes.

Production of these useful products is a major industry, and future growth is most promising. In 1957, some 38,500 tons of HF was used to produce 200 million pounds of fluorocarbons valued at 60 to 75 million dollars. Anticipating future growth, fluorocarbon production capacity already is rated at 410 to 490 million pounds (9). Producers are anticipating a fluorocarbon market of 230 million pounds in 1960 and 275 million in 1962. Stuewe (29) estimates that 67,000 tons of HF will be used in this industry in 1963. The refrigerant and aerosol industries each consume about 45 percent of the fluorocarbon production, plastics 3 to 5 percent, and miscellaneous, including export, the remaining percentage.



Almost all of the fluorocarbons are produced by the same general reaction. The basic reaction was discovered in 1892 by Swarts, a Belgian chemist, and was developed commercially in 1930 by Midgley and Henne for the manufacture of the Freon refrigerants. The reaction, expressed in its simplest terms, involves the replacement of chlorine in a suitable organic chloride with fluorine by means of a metallic fluoride or anhydrous HF. This is illustrated by the preparation of dichlorodifluoromethane (F-12),  $\text{CCl}_2\text{F}_2$ . In practice, carbon tetrachloride and anhydrous HF in a definite ratio are fed continuously to a heated reactor containing antimony



trifluoride and a catalyst. The volatile reaction products pass into a distillation column where the fluorocarbon is separated. By varying reactor conditions and using other chlorinated methanes and ethanes, a large group of fluorocarbons can be produced. The fluorocarbon work horses, or those produced in largest amount, are  $\text{CCl}_2\text{F}_2$ ,  $\text{CCl}_3\text{F}$ , and  $\text{CHCl}_2\text{F}$ . Approximately 1 ton of HF will produce 3 tons of fluorocarbon. Small amounts of fluorocarbons and derivatives are prepared also by the Simons electrochemical process (27, p. 414).

A cracking or pyrolysis process (20) on  $\text{CHClF}_2$  yields tetrafluoroethylene for teflon plastic manufacture, octafluorocyclobutane, and other fluorocarbon derivatives.

As the chemical names of the fluorocarbons are rather cumbersome for everyday usage, industry has developed general trade names and code symbols. The first commercial fluorocarbons were produced by the du Pont Company and were tradenamed Freon. Examples are F-11,  $\text{CCl}_3\text{F}$ ; F-12,  $\text{CCl}_2\text{F}_2$ ; F-13,  $\text{CClF}_3$ ; F-14,  $\text{CF}_4$ ; F-21,  $\text{CHCl}_2\text{F}$ ; F-22,  $\text{CHClF}_2$ ; F-112,  $\text{CCl}_2\text{FCCl}_2\text{F}$ ; F-113,  $\text{CCl}_2\text{FCClF}_2$ ; F-114,  $\text{CClF}_2\text{CClF}_2$ ; F-115,  $\text{CClF}_2\text{CF}_3$ ; and others. Other companies retained the same code numbers but prefixed their trade names such as Genetron (General Chemical Company), Isotron (Pennsalt Manufacturing Company), and Ucon (Union Carbide Chemicals).

### Refrigerants

The fluorocarbon gases are ideal as refrigerants because they are nontoxic, odorless, stable, noncorrosive, and have a low fire hazard. They are available in a wide range of boiling points, thus enabling refrigeration engineers more efficiently to match the machine to the application. For instance, demands differ widely between air conditioners (home, automobile, and commercial), refrigerators, and freezers. The average home refrigerator and cooler are charged with 1 to 2 pounds of refrigerant. About 75 percent of the refrigerant sales are for replacement purposes. With the trend toward hermetically sealed units, the demand for replacement gas will decrease. However, the market for air conditioning is far from the saturation point.

### Aerosols

Fluorocarbons were first used as inert propellants in the "bug bombs" produced for rapid fumigation purposes in World War II for the Armed Services. Out of this grew the fabulous aerosol industry which in 1958 (6) packed more than 100 products in 470 million units (dispensers) valued at 470 million dollars. Hair sprays, shaving lather, room deodorants, insect sprays, coatings, colognes, and perfumes accounted for more than 80 percent of the units sold. It was reported in 1957 that more than 60 percent (7) of the units were pressurized with an equivalent of about 43,000 tons of fluorocarbons.

The most important fluorocarbon propellants are F-12 ( $\text{CCl}_2\text{F}_2$ ) and F-11 ( $\text{CCl}_3\text{F}$ ) and mixtures thereof. Some use is made of fluorocarbons F-22 ( $\text{CHClF}_2$ ) and F-114 ( $\text{CClF}_2\text{CClF}_2$ ) to solubilize certain ingredients and to produce certain effects.

Producers of fluorocarbons still consider the aerosol field as an area of expansion. A manufacturer has estimated a market of 720 million aerosol units in 1962 and at least a billion units by 1968. Some producers agree that approval of fluorocarbons for food use by the Federal Food and Drug Administration would open a new market area in spite of possible severe competition from lower cost gases.

## Plastics

Teflon and Kel-F are the most important fluorinated plastics used in industry; in chemical language they are known as tetrafluoroethylene ( $\text{CF}_2=\text{CF}_2$ )<sub>x</sub> and tri-fluorochloroethylene ( $\text{CF}_2=\text{CClF}$ )<sub>x</sub> polymers, respectively. The basic raw materials are F-22 ( $\text{CHClF}_2$ ) and F-113 ( $\text{CCl}_2\text{FCClF}_2$ ). These plastics are nonflammable, insoluble in organic solvents, very stable to chemical agents, possess high thermal stability, and are excellent dielectric materials. They are fabricated into special gaskets, packings, pump liners, tubing, pipe, wire and cable coating, filter cloths, and many other items where their high cost is justified by the application. As teflon has a waxy surface with a low friction factor, it is molded into bearings having the property of natural lubrication, and it is used also as an antisticking coating on rollers and pans in food processing. Kel-F is quite transparent and is thermo-plastic.

Military agencies in the search for materials for use under severe conditions have stimulated plastic manufacturers to develop some special plastics. As these are costly, their production is small.

## Other Special Uses

A new development is being explored in which fluorocarbon gases will be used as foaming agents in the manufacture of urethane solid foams that have superior insulating properties. A stain repellent and fluorocarbon derivative, commercially known as "Scotchgard," is being used for coating furniture fabrics and men's suits. A variety of fluorocarbon liquids, oils, and greases are available as coolants, dielectrics, and lubricants.

Fluorocarbon surfactants, that is, agents that lower surface tension, are being used as levelling agents in polishes, oil-water mixtures, electroplating, etc. Bromotrifluoromethane ( $\text{CBrF}_3$ ) and dibromodibromomethane ( $\text{CBr}_2\text{F}_2$ ) are used as special fire extinguishers. Some coal tar dyes that contain fluorine find limited application as bright colors for cotton.

Medical science is using fluorosteroids for the treatment of arthritis and in the form of an ointment for skin irritations. Various organic fluorine compounds are being investigated extensively in cancer chemotherapy. Fluoroethane ( $\text{CF}_3\text{CHClBr}$ ) and Fluoromar ( $\text{CF}_3\text{CH}_2\text{OCH}_2 = \text{CH}_2$ ) are being tested extensively as new anesthetics. Some tranquilizers and a diuretic contain fluorine in their composition. Indoklon ( $\text{CF}_3\text{CH}_2\text{OCH}_2\text{CF}_3$ ) is being tested as a pharmacconvulsive agent in mental therapy.

A fluorinated compound is being used in an effort to control the lamprey pest which has practically destroyed commercial fishing in the Great Lakes. Some interest in the use of fluoroorganic materials as insecticides, weed killers, shock absorber liquids, and selective solvents has been reported.



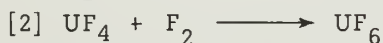
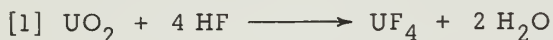
### Petroleum Alkylation

During World War II the HF process for producing high-octane blending components for gasoline was developed. The HF functions as a catalyst for the conversion of olefins and isoparaffins into an alkylate that consists of a mixture of isomers of heptane, octane, etc. As the process is catalytic, very little make up HF is needed to maintain the reactors at their capacity. Unconfirmed reports indicate that some reactors use 50 tons of anhydrous HF. Although the sulfuric acid process still produces 80 percent of the alkylate, the HF process is showing a small, steady increase.

### Atomic Energy

Uranium 235, a key nuclear fuel component in atomic energy, is found in a very small amount along with a preponderance of uranium 238 in natural occurring uranium ore. The separation and concentration of the  $U^{235}$  isotope posed the problem of finding a thermally stable uranium compound with a high vapor pressure at room temperature. Uranium hexafluoride ( $UF_6$ ) with a sublimation point of  $56^\circ C$  met these specifications. The isotopes are conveniently separated by submitting the  $UF_6$  vapor to a diffusion process.

The  $UF_6$  feed material for diffusion, in terms of fluorine chemistry, is produced by a two-step process. Uranium dioxide is treated with anhydrous HF to form the so-called green salt,  $UF_4$ .



The green salt is then fluorinated with fluorine gas to uranium hexafluoride. As enriched uranium metal is used as the reactor fuel, it is necessary to reduce the  $U^{235}F_6$  to the metal. Part of the fluorine is recovered and returned as 70 percent aqueous hydrofluoric acid to the HF merchant for other purposes.

### Elemental Fluorine

Although Moissan in 1886 succeeded in preparing fluorine as a free element by the electrolysis of potassium acid fluoride, it was not until World War II that the problem of large-scale production was solved. As pointed out, the development of an industrial fluorine cell was a necessity in the production of an atom bomb.

Commercial fluorine cells still use potassium acid fluoride as an electrolyte. However, by feeding HF to the cells to maintain the proper composition, continuous fluorine generation is achieved. A recently installed plant (8) has been reported to have a fluorine capacity of 364 pounds per hour with a possible expansion to 550 pounds per hour. Liquid fluorine is now available in tank truck tonnages.

Besides its use in making  $UF_6$ , liquid fluorine is being considered for use as an oxidizer in rocket engines. Rocket velocity and range are determined by the specific impulse or thrust of a fuel and oxidizer. Combined with existing fuels, liquid fluorine (5, 31) has the highest specific impulse of bipropellant systems. Because of its extreme reactivity, many problems will have to be solved and a long research road lies ahead.

Very little fluorine is used for other purposes. Sulfur hexafluoride, prepared by direct combination of sulfur and fluorine, is an inert gas that is used as a dielectric in x-ray tubes. Higher metallic fluorides ( $CoF_3$ ,  $AgF_2$ ,  $MnF_3$ , etc.)

and halogen fluorides ( $\text{ClF}_3$  and  $\text{BrF}_3$ ), useful in special fluorinations, are prepared only by oxidation with fluorine gas. An interesting application of chlorine trifluoride,  $\text{ClF}_3$ , is in the perforation and cutting of pipe in oil wells below the earth's surface (4).

### Other Inorganic Fluorides

In addition to the fluorides discussed above, there are a number of other useful common compounds. The total production of these per year is estimated by Stuewe (29) to be about 14,500 tons.

Most of the common inorganic fluorides are prepared by reacting aqueous hydrofluoric acid with the corresponding carbonates, oxides, or hydroxides. The bifluorides or acid fluorides are formed with an excess of acid. Anhydrous HF is used to prepare the water-sensitive fluorides such as boron trifluoride and others.

Sodium fluoride is used in water fluoridation and in manufacture of rimmed steel, opaque glass, toothpaste, wood preservatives, and insecticides. About 6,000 tons appear to be the annual production. Some sodium fluoride is obtained also from silicofluorides. Only very small amounts of ammonium and potassium fluorides are used, the potassium salt being used in organic syntheses and solders.

The ammonium, potassium, and sodium bifluorides have many diverse uses. They all can be used in the frosting and etching of glass. Both the ammonium and sodium salts are used as laundry sourers and iron stain removers. Sodium bifluoride is used in the acid treatment of steel prior to electroplating for tin cans. The ammonium salt is utilized also in the treatment of oil wells, as an antiseptic and preservative, for the removal of scale in boilers and auto radiators, and in the extraction of beryllium. Potassium fluoride is used in the production of fluorine gas and in solder compositions. Approximately 2,000 tons each of the ammonium and sodium salts are used annually whereas 300 tons is a close proximation for the potassium salt.

Production of boron trifluoride ( $\text{BF}_3$ ) is estimated at 2,000 tons a year. It is available in cylinders or in combination with certain organic solvents, and is very corrosive in the presence of moisture. Its chief use is in the manufacture of coumarone-indene, petroleum resins, and lube oil additives, and as a catalyst in organic syntheses.

Annual production of fluoboric acid ( $\text{HBF}_4$ ) and its fluoborate salts, generally prepared from boric acid or borax with hydrofluoric acid, is less than 1,000 tons. The acid is used in the cleaning and pickling of metals, electropolishing of aluminum, and in organic syntheses. Because of high anode and cathode efficiency and a fine-grain deposit, the acid and certain salts are used in baths for specialty electroplating such as cadmium, chromium, copper, indium, iron, lead, lead-tin, nickel, silver, tin, and zinc. Ammonium fluoborate is added to the molds in magnesium casting to prevent oxidation. The sodium salt is used in the heat treatment of aluminum alloys to prevent blistering and crack formation and as a flux in non-ferrous metallurgy. The use of potassium fluoborate in the manufacture of brazing and soldering fluxes and in grinding wheels has been reported.

Silicon tetrafluoride ( $\text{SiF}_4$ ) gas has been useful in sealing off downhole water zones during air and gas drilling (30). The dry gas upon injection into a well penetrates into the permeable water zone where it hydrolyzes to a fluosilicic acid gel thus plugging the pore passages.

Atomic and rocket age demands for new materials have stimulated fluorine chemical producers to offer many fluorides, some of which were considered Ivory

Tower rarities 20 years ago. Sales advertisements have been noted on the fluorides of antimony, barium, bismuth, cadmium, caesium, chromium, cobalt, copper, iron, lead, lithium, magnesium, manganese, mercury, molybdenum, nickel, rare earth fluorides, rubidium, selenium, silver, strontium, tin, titanium, tellurium, tungsten, zinc, zirconium, and many double fluorides of chromium, iron, tantalum, titanium, zinc, and zirconium in the form of ammonium, potassium, and sodium complexes.

### Fluosilicic Acid and Salts

No discussion on the uses of fluorine compounds is complete without mention of fluosilicic acid and its salts called fluosilicates or silicofluorides. They can be prepared from low-grade fluorspar and sulfuric acid. However, they are available at low cost as a by-product from domestic fertilizer phosphate rock acidulation and through tonnage importation from Europe and Japan. Under these circumstances it is not economically feasible to produce them from fluorspar.

Fluosilicic acid ( $\text{H}_2\text{SiF}_6$ ) is used in water fluoridation, electroplating, as a concrete hardener, disinfectant, wood preservative, and in the manufacture of metallic fluosilicates and fluorides. The production of sodium fluosilicate ( $\text{Na}_2\text{SiF}_6$ ) in 1955 was 18,000 tons, almost three times as much as the rest of the salts combined. Approximately 40 percent of the sodium salt is used in water fluoridation, the remainder being used as a laundry sour, in enamel and opal glass, insecticides, and foam rubber. The potassium salt ( $\text{K}_2\text{SiF}_6$ ) is used in enamels, light metal fluxes, and synthetic mica.

Zinc fluosilicate is used as a wood preservative, and like the magnesium salt, is used also as a laundry sour and concrete hardener. The chief uses for ammonium fluosilicate are in water fluoridation, mothproofing, and as a laundry sour. Used as insecticides and in ceramics as opacifying agents are the barium and calcium salts. Lead fluosilicate appears in electrolytic lead refining and plating. Occasionally salts of aluminum, iron, nickel, and silver are mentioned with special uses.

## DIRECTORY OF ILLINOIS FLUORSPAR MINES AND MILLS

The Illinois fluorspar mining industry comprises mines operated in connection with processing mills, mines operating more or less continuously but having no mills, and small mines worked periodically. Below are listed those companies with mills and companies without mills that mined more than 3,000 tons of ore in 1957.

### Companies with Mills

#### Aluminum Company of America, Rosiclare:

Mill: 400-ton flotation-heavy media mill, Rosiclare

Mine: Fairview-Blue Diggings Mine, Rosiclare

#### Minerva Oil Company, Fluorspar Division, Eldorado:

Mills: 325-ton flotation mill, Mine No. 1, Cave in Rock

750-ton flotation-heavy media mill, Crystal Mine, Route 1,  
Elizabethtown

Mines: Mine No. 1, Cave in Rock

Crystal and Victory Mines, Route 1, Elizabethtown

Jefferson Mine, Route 4, Golconda

Rose Creek Mine, near Herod

Ozark-Mahoning Company, Mining Division, Rosiclare:

Mill: 500-ton flotation mill, Rosiclare

Mines: Deardorff, W. L. Davis No. 2, North Green, East Green, Hill-Ledford, Oxford, and Shafts No. 2, No. 3, No. 5, No. 11, and No. 16, all near Cave in Rock

Rosiclare Lead and Fluorspar Mining Company, Rosiclare:

Mill: 300-ton flotation-heavy media mill

Mine: Rosiclare Mine (idle)

Mackey-Humm Fluorspar Mining Company, Box 336, Golconda:

Mill: 100-ton heavy media mill

Mine: Mackey-Humm Mine, Humm's Wye (idle)

#### Companies without Mills

Egyptian Mining Company, Rosiclare: Empire Mine, near Eichorn.

Goose Creek Fluorspar Mining Company, Cave in Rock: Goose Creek Mine, near Sparks Hill.

Hicks Creek Fluorspar Mining Company, Elizabethtown: Douglas Mine, near Eichorn.

Hoeb Mining Company, Cave in Rock: Hoeb Mine, near Sparks Hill.

J. W. Patton and Sons, Elizabethtown: Crabb Mine, near Eichorn.

Redd Mining Company, Route 4, Golconda: Hamp Mine, near Hicks.

Ridge Mining Company: Ridge Mine, near Karbers Ridge.

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CIRCULAR 296

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